Chapter 1

Introduction

Liquid crystals are intermediate states between the crystalline solid and the amorphous liquid[1]. These states are strongly anisotropic in some of their properties like a crystal and at the same time exhibit some fluid properties as well. Transitions to these intermediate states may be brought about by heating or cooling (thermotropic mesomorphism) or by the effect of solvents (lyotropic mesomorphism). In general, molecules of mesogenic compounds are highly anisotropic, usually long and narrow. However, it was discovered by Chandrasekhar et al [2], that pure compounds of disc-shaped molecules can also show liquid crystallinity. This thesis deals with only thermotropic liquid crystals of rod-like molecules.

1.1 Classification of thermotropic liquid crystals

Thermotropic liquid crystals of rod-like molecules are broadly classified[3] into three types: *nematic, cholesteric* and *smectic.*

1.1.1 Nematic

The nematic (N) phase has a high degree of long range orientational order, but no long range translational order (Figure 1.1(a)). The molecules are spontaneously oriented with their long axes approximately parallel to some common axis termed as the director $\vec{n}$. However, the preferred direction usually varies from point to point in the medium, but a homogeneously aligned specimen is optically uniaxial, positive and strongly birefringent.

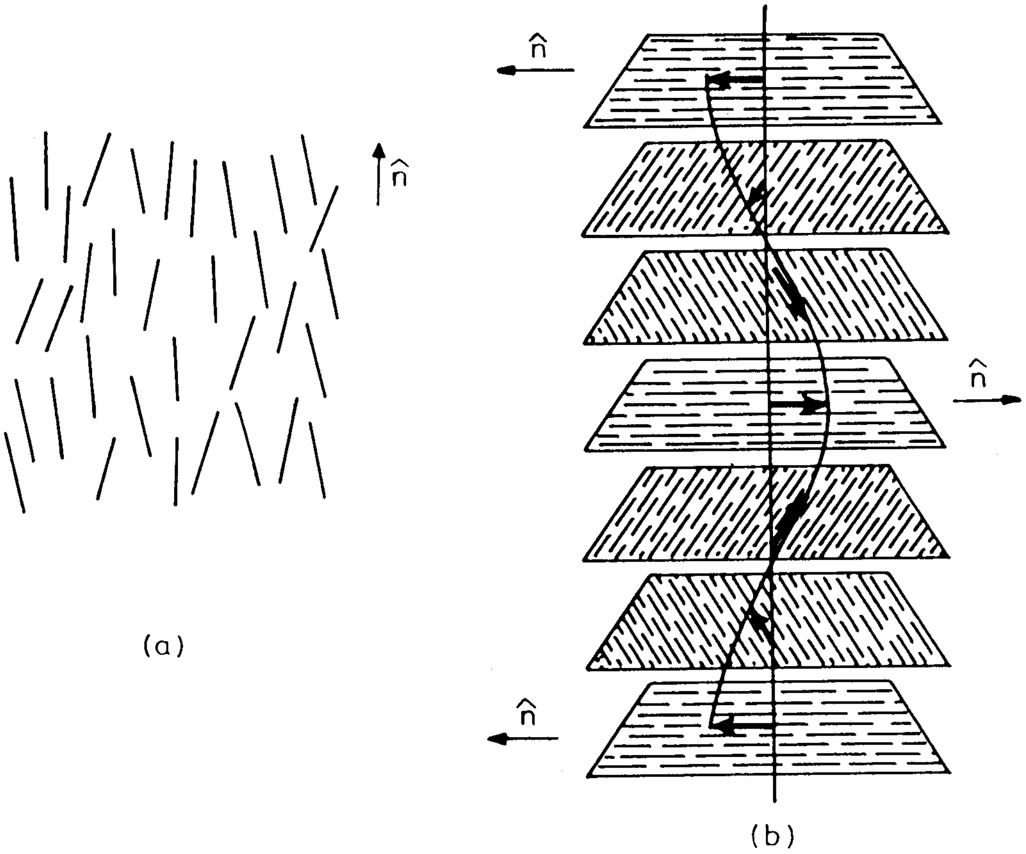

Figure 1.1: Molecular arrangement in (a) nematic, (b) cholesteric. $\hat{n}$ denotes the director.

1.1.2 Cholesteric

The cholesteric mesophase is a chiral version of the nematic phase, observed in materials with optically active molecules. As a result of this, the structure has a screw axis superimposed normal to the preferred molecular direction (Figure 1.1(b)). However, a racemic mixture(of right- and left- handed chiral molecules) will have a helix of infinite pitch which corresponds to the true nematic. The spiral arrangement of the molecules in the cholesteric mesophase is responsible for its unique optical properties, viz., selective reflection of circularly polarised light and a rotatory power about thousand times greater than that of an ordinary optically active substance.

1.1.3 Smectic

Smectic phase is characterised by a layered structure in addition to the orientational order of the nematic phase. Depending on the molecular arrangements within the layer and the extent of inter-layer correlations smectic mesophases are classified into different types.

Here we describe the structures of those smectic phases, dealt with mainly in the work presented in this thesis, viz., smectic A, smectic C, its chiral modification smectic C*, and smectic B phases.

Smectic A

In the smectic A (A) phase the molecules are upright with their centres irregularly spaced within each layer in a ' liquid -like ' fashion (Figure 1.2(a)). This arrangement has been described as a one-dimensional mass density wave with the wavevector parallel to the director[4,5,6]. The inter-layer correlations exhibit quasi-long range order. The Landau-Peierls instability[7] arising in such a system having one-dimensional translational order in three- dimensional space should manifest itself as a quasi Bragg X-ray line profile[8]. Als-Nielsen et al[9] have shown that this is indeed the case. The idealised picture of smectic A phase shown in Figure 1.2(a) is far from accurate. A more realistic molecular picture[10] is shown in Figure 1.2(b).

Smectic C

The smectic C (C) phase is a tilted version of the A phase i.e., the molecules which are upright in A, are now tilted with respect to the layer normal (Figure 1.3). While the A phase is optically uniaxial, the C phase is optically biaxial.

Smectic C*

If the molecules are optically active in the C phase then they form a chiral smectic C or smectic C* (C*)phase[11]. Due to the presence of chirality the azimuthal angle of the tilted molecules precesses from one layer to another giving rise to a helicoidal structure (Figure 1.4). The pitch of the helix is given by $\frac{2\pi}{q}$, where q is the wave vector of the helix. By symmetry arguments (to be discussed in Chapter 4) the C* phase exhibits ferroelectric properties, i.e., each layer shows a non-zero spontaneous polarisation P_S perpendicular to the direction of the tilt and the layer normal $\vec{n}$ [12]. However, the presence of the helix averages out the

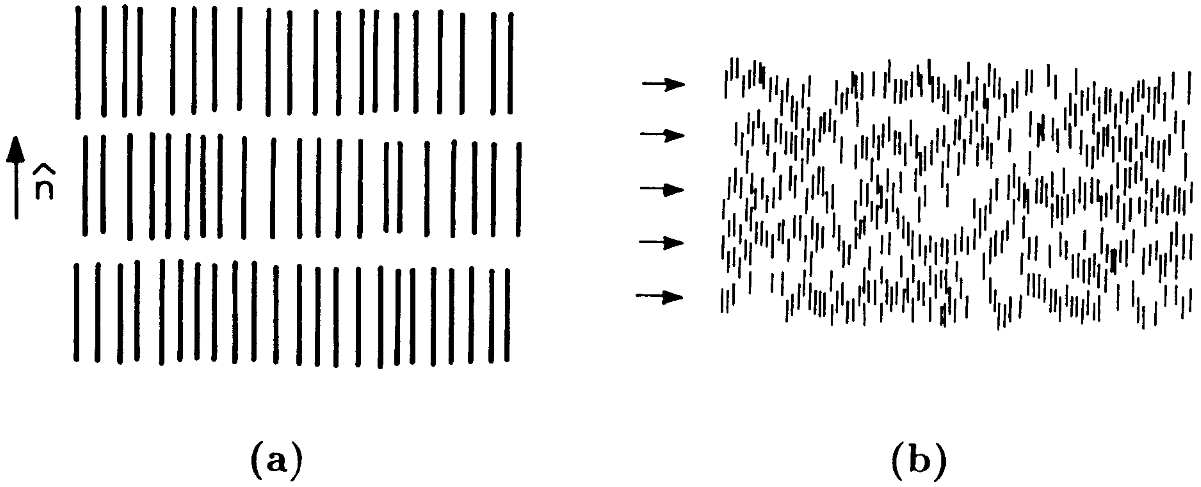

Figure 1.2: (a) Molecular arrangement in smectic A phase. (b)A realistic distribution of molecules in the smectic A phase. The arrows in the figure denote the crests of the density wave.(From ref.[10])

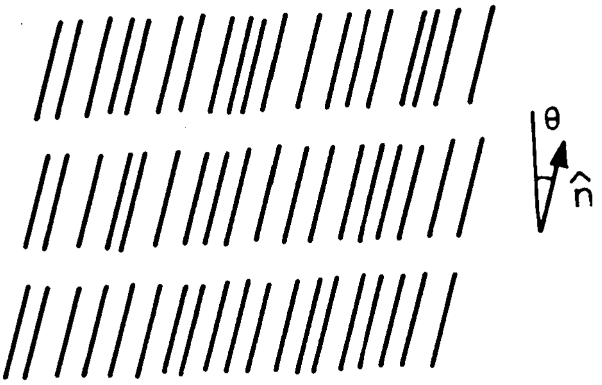

Figure 1.3: Molecular arrangement in smectic C phase.

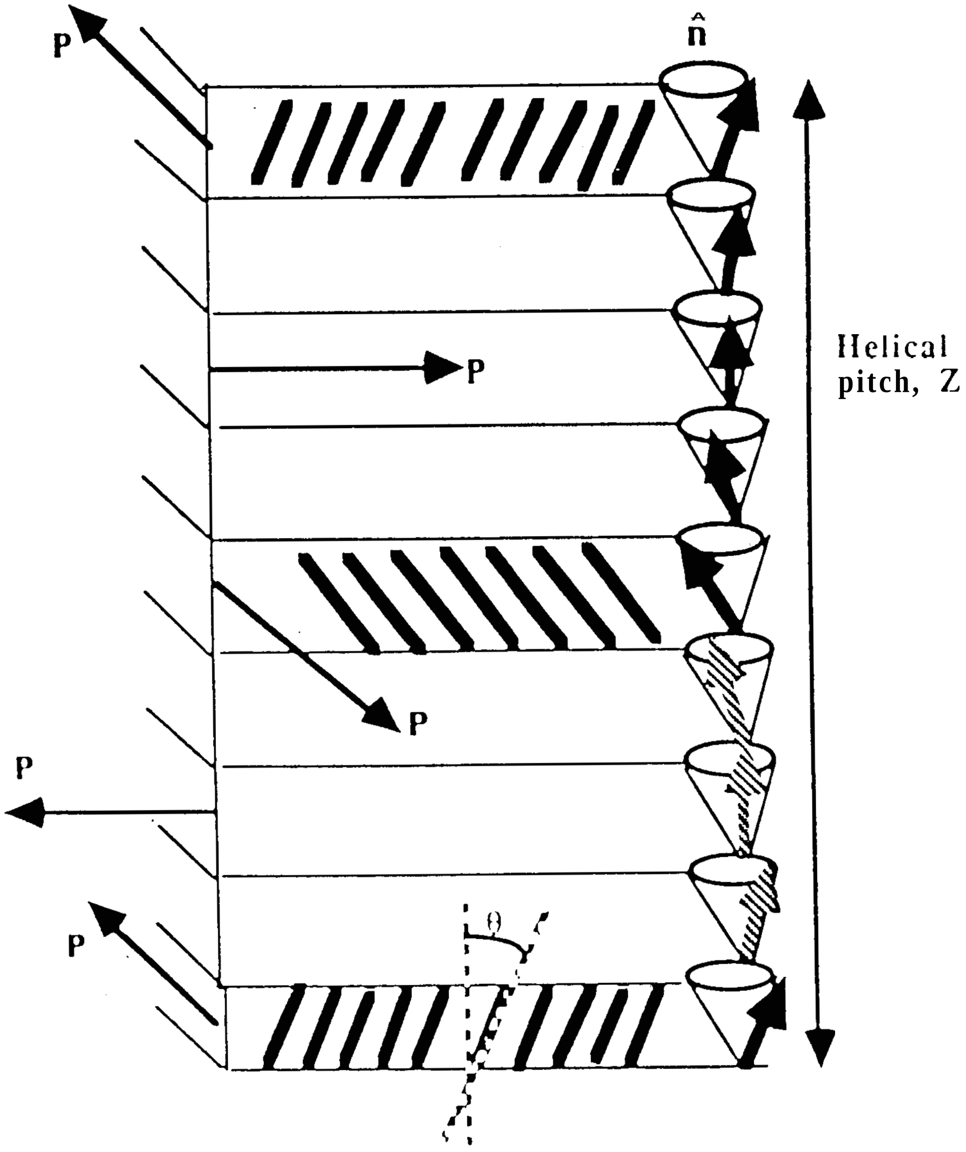

Figure 1.4: Twisted smectic C* phase.

macroscopic polarisation to zero. To obtain a non-zero macroscopic polarisation the helix has to be unwound by an external field, such as electric field[13] or shear[14] or by surface interactions[15]. Figure 1.5 shows the structure of an unwound smectic C* phase.

Twist Grain Boundary(TGB) or A* phase

Recently, Renn and Lubensky[16] have extended the analogy between the normal-superconducting transition in metals and the nematic-smectic A transition [6] to predict an analogue of the Abrikosov flux lattice[17] in liquid crystals containing chiral molecules. This new phase termed as the Twist Grain Boundary phase is recognised to be identical[19] to the A* phase discovered by Goodby et al[18]. According to the model given by Renn and Lubensky, the TGB phase consists of a regular array of twist grain boundaries composed of regularly spaced screw dislocations with axes that rotate from one grain boundary to the next giving rise to a helix. The helical axis direction in the TGB phase is parallel to the layer planes (and normal to the director as in the cholesteric). The configuration of molecules between the grain boundaries is essentially identical to that of the A phase with regularly spaced layers separated by a layer thickness d. (The schematic representation of a TGB phase is given in Figure 5.2–Chapter 5).

Smectic B

In the smectic B phase the molecules are upright and hexagonally close packed. Two types of smectic B phases have been identified, viz., the hexatic B and

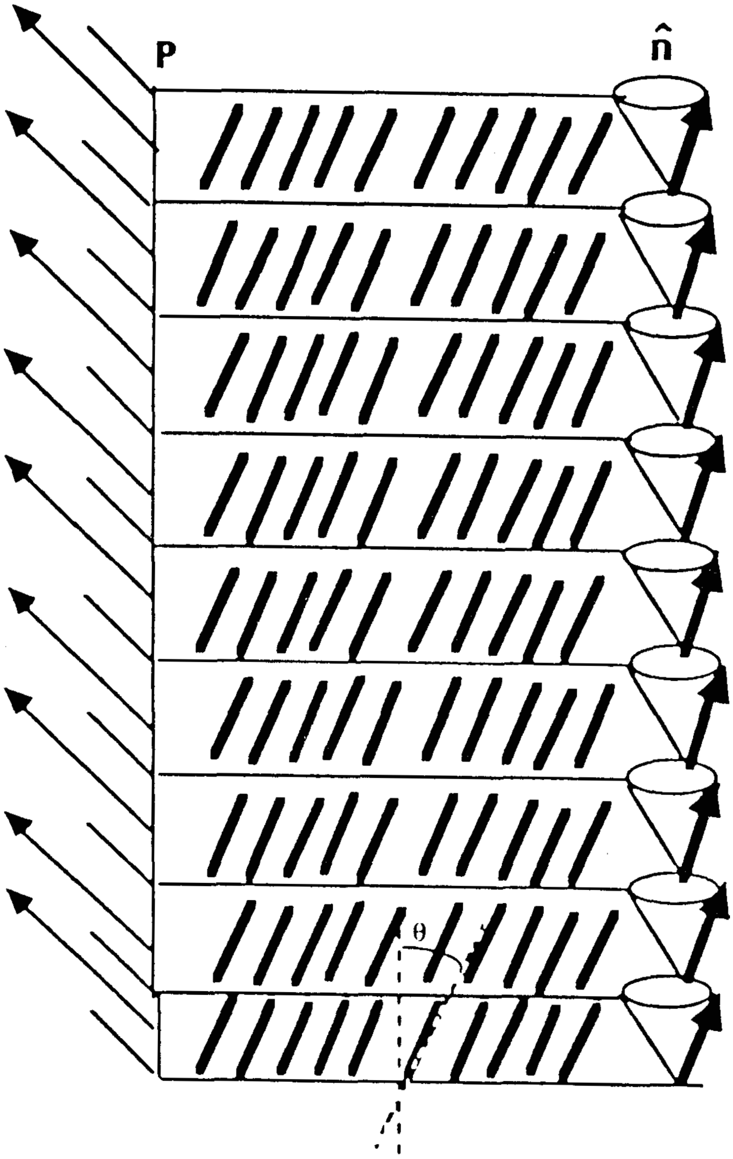

Figure 1.5: Unwound smectic C* phase.

the crystal B. The hexatic B(B_{hex}) phase has long range bond orientational order(the bond orientational order is defined in Chapter 6), short range in-plane positional correlation and no interlayer correlation. The crystal B(B_{cry}) phase has long range in-plane correlation and a high degree of interlayer correlation like a 3D crystal.

For materials having nematic and smectic mesophases the typical sequence of phase transitions on cooling the sample is usually as follows:
Isotropic - N - A - C - B - solid. Exceptions to this rule, in which materials exhibit reentrant phases, are known but we do not deal with such cases in our studies.

The present thesis deals mainly with the experimental studies on the smectic A-smectic C or the smectic A-smectic C* phase transition. The experimental methods employed to measure the thermal variation of different material parameters across this transition are also described. The results obtained, in most of the cases, have been compared with different theoretical models for the A-C or A-C* transition. The thesis also describes experimental studies on a novel phase diagram involving the twist grain boundary phase in the vicinity of a virtual Ch-A-C* point, and on high pressure studies on materials exhibiting either hexatic B or crystal B phases. The overall contents of five chapters are summarised in the following sections.

1.2 First order Smectic A-Smectic C*/ Smectic A-Smectic C transition

The Smectic A-Smectic C (A-C) transition is described by a complex order parameter [20], $\psi=\theta e^{i\phi}$, where θ is the magnitude of the tilt angle and ϕ is the azimuthal angle. Since ϕ can be chosen arbitrarily, θ itself can be taken as the order parameter in the free energy expansion for the A-C transition. In the case of the A-C* transition, owing to the existence of ferroelectricity one should, in principle, consider both θ and the spontaneous polarisation P_S as order parameters. But experimental evidence[21,13] indicated that the transition is brought about by the same intermolecular forces producing the C phase and not by the ferroelectric coupling between the permanent dipoles. Therefore P_S becomes a secondary order parameter for the A-C* transition and the tilt angle θ the primary order parameter. Thus the basic physics of the A-C* transition may be expected to be same as that of the A-C transition.

From symmetry considerations, A-C/A-C* transition can either be first order or second order. But experimentally, this transition was generally found to be second order. Lien and Huang[22] predicted that this transition can be driven to become first order by the large fluctuations of a nearby A-I transition. However, no conclusive proof of a material having a first order A-C or A-C* transition had been reported so far.

Chapter 2 describes high precision X-ray measurements of the tilt order parameter on a ferroelectric material 4- (3-methyl -2- chloropentanoyloxy) -4' -heptyloxy biphenyl (MCP7OB) (having a high $P_S \sim 300$ nC/cm^2)[23] which led to the first unambiguous observation of a first order A-C* transition. The experiments have been carried out using a computer controlled Guinier diffractometer (Huber 644). An aligned A phase was obtained by cooling the sample at a very slow rate($\sim$ 300 mK /h) from isotropic to the A phase in the presence of a 2.4 T magnetic field. The aligned sample was later transferred along with the temperature controlled oven to the goniometer head of the diffractometer. The precision in the determination of the wave vector was $2\text{x}10^{-4}$ $\AA^{-1}$. The resolution in the equatorial direction was $3\text{x}10^{-1}$ $\AA^{-1}$. The temperature was maintained to a constancy of ± 5 mK. Layer spacing as a function of temperature has been measured both in the A and C* phases. The tilt order parameter was calculated using the equation

$$\theta = \cos^{-1}(d_{C^*}/d_A)$$

where d_{C^*} and d_A are the layer spacings in the A and C* phases respectively. The results obtained shows that the tilt angle 0 has a discontinuous jump at the transition to the A phase. Also, in the transition region, the low angle scattering spectrum shows two peaks associated with the density modulations of both A and C* phases indicating a two phase region. These results clearly indicate that the A-C* transition in this material is first order.

Chapter 2 also describes the experimental studies carried out in order to understand the origin of a first order transition in such materials. Huang has compiled[24] all the available data on the A-C/A-C* transition and found a systematic trend with respect to the temperature range of the A phase. The calorimetric measurements indicated the possibility of finding a first order

A-C/A-C* transition by shrinking the temperature range of the A phase. In a recent study, Liu et al[25] have argued that reducing the temperature range of the A phase alone may not make the transition first order, but an additional parametes, viz., the magnitude of the transverse dipole moment of the constituent molecules has a strong effect on the order of the transition. A more systematic study in this direction was essential to understand the nature of this transition. With this in mind, X-ray diffraction studies have been carried out on two other liquid crystalline systems. One is a homologous series of a non-ferroelectric material(TBnA) with a weak transverse dipole moment[26] and another a ferroelectric material(A7[*l*] for short) with a strong transverse dipole moment. In the former, the temperature range of the A phase varies with the chain length and the experiments have been done on 10th(TBDA), 8th(TBOA) and a 10 mol% mixture of TBOA in TBDA. The results obtained can be summarised as follows: if the transverse dipole moment of the constituent molecule is strong, materials with a large range of A phase can show first order A-C/A-C* transition. For materials with weak transverse dipole moment, the range of the A phase has to be much smaller for the same effect to be seen.

1.3 Mean-field to Tricritical cross-over behaviour near the A-C* Tricritical Point

From the point of view of critical phenomena, an important feature to be noted is that as some material parameters are varied, the order of the transition changes from first to second. The observation of the switch-over point, termed as the tricritical point(TCP)[27], on the A-C (or A-C*) line, had eluded experimenters despite considerable effort.

Although it was initially proposed[20] that the A-C (or A- C*) transition should exhibit helium-like critical behaviour, subsequent studies[28] have clearly shown that A-C (or A-C*) transition is mean-field-like with a large sixth order term[29] in the Landau free energy expansion. The presence of the sixth order term implies that the transition is always close to a mean-field tricritical point with a concomitant existence of a 'cross-over' behaviour from a mean-field-like region to a tricritical-like region[30].

Chapter 3 describes high resolution X-ray experiments which led to the first observation of a A-C* TCP and the associated cross-over behaviour. The experimental work in this direction was started after finding a first order A-C* transition in a ferroelectric material MCP7OB, discussed in Chapter 2. Preliminary results of X-ray measurements showed that adding another material, 4 -heptyloxy -4' -decyloxybenzoate (7OPDOB for short), with a known second order A-C transition drives the first order transition to second order leading to a TCP. High resolution tilt angle measurements were done on several mixtures of the two materials on the second order side of the tricritical point. A novel method of analysing the data is described, which brings out beautifully the explicit characteristics of the cross-over behaviour. The results clearly show a mean-field to tricritical cross-over behaviour, with the mean-field range shrinking to zero at the TCP. It is also observed that the data for a mixture very close to the TCP yield a tricritical exponent of 0.25 for the tilt angle as is to be expected theoretically[1,31].

1.4 Polarisation–Tilt Coupling and thermal variation of Pitch in the Chiral Smectic C phase

In spite of considerable experimental and theoretical work done in characterising the ferroelectric properties in the chiral smectic C phase, the nature of the coupling between the magnitude of the tilt, θ, and spontaneous polarisation P_S has not been well understood. A simple theoretical approach[32] expects the P_S and θ to be coupled in a linear way. Also it predicts the helical pitch p to be invariant with respect to temperature. However, the experimental observations do not agree with these predictions. Especially, the ratio $\frac{P_S}{\theta}$ is weakly dependent on the temperature deep in the C* phase, but shows a strong variation close to the A-C* transition temperture. Similarly, far below the transition, the helical pitch varies slowly with temperature and shows a maximum below the transition temperature.

Based on the experimental observations mainly on p-decyloxy benzylidene p- amino-2- methylbutyl- cinnamate (DOBAMBC), extended mean-field(EMF) models [33,34] with as many as eleven expansion coefficients were proposed. In these models, in addition to the terms considered in the simple model, a sixth order term in tilt[29,35] and a biquadratic term in polarisation-tilt coupling[36, 33] were also taken into account. Most of the measurements[37,38,39] that have been done so far present results wherein not enough attention has been given to the region close to the A-C* transition. The few high resolution studies[34,40] have been carried out on materials with low polarisation. This necessitated a systematic study to understand the nature of the P_S-θ coupling and the thermal variation of pitch.

Chapter 4 presents a detailed study of temperature variation of P_S, θ and p carried out on three different materials having different degrees of polarisation. The measurements of spontaneous polarisation have been done using the Diamant Bridge technique[41] and the p by standard optical diffraction method[42,43]. The details of these are also given in Chapter 4. The experimental results obtained are analysed in the frame work of an extended mean field(EMF) model[33] as well as a microscopic model[35,44] proposed recently. One of the quantities that plays a major role in the predictions of the EMF model is the effective coupling coefficient β_c, defined as the ratio of the coefficients of the bilinear to biquadratic P_S-θ coupling terms. This coupling coefficient is expected to determine the nature of the thermal variation of $\frac{P_S}{\theta}$ ratio and p. The analysis shows that the magnitude of β_c does determine the temperature dependence of $\frac{P_S}{\theta}$ and pitch. Also, the nature of the coupling between P_S and 0 is dependent on the proximity to the A-C* transition, i.e., the influence of the biquadratic term is small near the T_{AC^*} and large far away from it. These features are generally in good agreement with the predictions of the EMF model. The experimental data are also compared with the predictions of a microscopic model[44] which is based on a single particle potential. The results of the analysis brings out the similarity in the interpretation of the data in terms of the two models.

1.5 Phase Diagram involving the Twist Grain Boundary Phase in the vicinity of a virtual Cholesteric-Smectic A-Smectic C* point.

A phenomenological model given by Chen and Lubensky[45] has been very successful in explaining the experimental observations near a nematic-smectic A-smectic C (NAC) multicritical point[46]. Recently Renn and Lubensky have generalised[16,47] this model to describe the effects of chirality on the NAC point and its immediate neighbourhood. Depending on the strength of the chirality, the theory expects different types of topologies for the meeting point. When the chirality is zero one gets the well known nematic-smectic A-smectic C (N-A-C) multicritical point[46]. For the finite chirality case, the theory gives two alternatives depending upon whether the system behaves like a type I superconductor or type II superconductor. In the former case, the meeting point Cholesteric-smectic A-smectic C* (Ch-A-C*) would be a critical end point, where a line of second order transitions is truncated by meeting a line of first order transitions. In the latter case, the meeting point is preempted by the appearance of a new type of phase, viz., the Twist Grain Boundary (TGB) phase which is the liquid crystal analogue of the Abrikosov flux lattice[17] in a type II superconductor. The TGB phase was identified[19] to be the same as the A* phase discovered by Goodby et al [18]. But neither in this work nor in the subsequent ones[48] was the TGB phase found where it was expected to occur, viz., near a Ch-A-C* meeting point.

Chapter 5 descibes the experimental studies on a novel phase diagram which shows the existence of the TGB phase near the Ch-A-C* meeting point. Optical microscopic measurements have been carried out on binary mixtures of 4-(2'- methyl butyl) phenyl 4' -n-octyl biphenyl -4-carboxylate (CE8)[49] and 4-n-dodecyloxy biphenyl-4'- (2' -methyl butyl)benzoate (C12)[50]. In CE8, the A phase intervenes between Ch and C* transition. In C12 there is a direct Ch to C* transition. In the temperature- concentration (T-X) phase diagram, (where X is the weight% of C12 in CE8), it is seen that for $0.32 < X < 0.7$ there appears an intermediate phase signalled by the 'filament' texture which is characteristic of the TGB phase[18]. Differential Scanning Calorimetric(DSC) measurements have been carried out on X=0.6 and 0.66 using Perkin Elmer DSC-4. The DSC scans showed the presence of this phase in both the mixtures. A necessary feature of the TGB phase is the simultaneous existence of the layering as well as a macroscopic helical structure with its axis parallel to the layer planes. X-ray layer spacing measurements carried out on the same two mixtures showed the presence of layering in the TGB phase. To get a quantitative information about the helical structure, selective reflection measurements using VIS/IR spectrometer (Hitachi U3400) have been carried out. The results indeed showed the presence of helical structure in the TGB phase. All these results clearly indicate the presence of the TGB phase in the vicinity of a virtual Ch-A-C* meeting point.

1.6 High Pressure studies on some liquid crystals exhibiting Hexatic B/Crystal B phases

The observation of pressure induced mesomorphism[51] is one of the most significant early results in the area of high pressure studies on liquid crystals. This led to the first observation of triple points(a triple point is the meeting point of three first order lines) in single component systems at high pressures[52,53]. It was also found that in some other cases pressure can supress mesophases[54] and this again leads to important consequences. The observation of tricritical points for the smectic A-nematic (or cholesteric)[55,52] and transition at high pressure revealed the potentialities for multicritical phenomena. So far very few multicritical points have been observed at high pressures. These are the nematic-smectic A-smectic C (N-A-C) multicritical point[46] and its reentrant version, the reentrant nematic-smectic C-smectic A (RN-C-A) multicritical point[56].

In Chapter 6, results of high pressure studies, undertaken on different liquid crystalline systems, exhibiting either hexatic B or crystal B phases, with a view to observing new kinds of multicritical points, have been described. The three materials, N- (4-n- butyloxy benzylidene) -4-n-octylaniline (4O.8), N- (4-n- heptyloxy benzylidene) -4-n- heptylaniline (7O.7) and 50 mol% mixture of 4 -butyloxy -4' -decyloxybenzoate (5OPDOB) and 4 -heptyloxy -4' -decyloxybenzoate (7OPDOB), have nematic-smectic A-crystal B, smectic A-smectic C-crystal B and smectic A-smectic C-hexatic B phase sequences respectively at room pressure. The experiments have been carried out using an optical high pressure cell up to pressures of about **3** kbar. The precision in measuring the pressure was ± 0.8 bar and temperature ± 20 mK. The details of the set up is given in Chapter 6. In the case of 4O.8, the A phase gets bounded at high pressures leading to a N-A-B,,, critical end point. In the case of 70.7 also, the intermediate phase, i.e., C phase gets bounded resulting in a A-C-B,,, CEP. Interestingly, when the B_{cry} phase is replaced by B_{hex} phase (50 mol% of 5OP-DOB in SOPDOB), a totally different topology of the P-T diagram is observed. Here again the C phase gets bounded at high pressures giving rise to a A-C-B_{hex} meeting point. Three possibilities have been proposed for this meeting point; they are (i)a mean-field bicritical point(the meeting point of two second order lines and a first order boundary) (ii)a triple point (iii)a new type of multicritical point(i.e., the meeting point of three second order boundaries). Thus the results of high pressure studies on materials exhibiting hexatic or crystal B phases have led to the observation of a N-A-B_{cry} CEP, A-C-B_{cry} CEP and a A-C-B_{hex} meeting point.

Most of the results described in this thesis have been published in the following papers.

1. Evidence of a first order smectic A - smectic C* transition and its approach to tricritical behavior (in collaboration with B. R. Ratna, R. Shashidhar, S. Krishna Prasad, Ch. Bahr and G. Heppke), *Phys.Rev.* A 37,1824 (1988).
2. Mean-field to Tricritical cross-over behavior near the smectic A - smectic C* Tricritical point (in collaboration with R. Shashidhar, B. R. Ratna, S. Krishna Prasad, Ch. Bahr and G.Heppke), *Phys. Rev. Lett. 61, 547* (1988).
3. The temperature range of the smectic A phase and its effect on the smectic A - smectic C transition (in collaboration with S. Krishna Prasad, V. N. Raja, D. S. Shankar Rao and M. E. Neubert.) *Phys. Rev.* A *42,* 2479, (1990).
4. Mean-field tricritical behavior of the smectic A -smectic C* transition in binary mixtures of the D and L forms of a ferroelectric liquid crystal (in collaboration with S. Krishna Prasad, R. Shashidhar, B. R. Ratna, Ch. Bahr and G. Heppke) Presented at the 13th International Liquid Crystal Conference, Vancouver, Canada (1990).
5. On the variation of pitch and polarisation - tilt coupling in chiral smectic C (in collaboration with S. Krishna Prasad), Mol. *Cryst. Liq. Cryst.* 202, 91 (1991).

6. Smectic A -Smectic C - Hexatic B meeting point at high pressure - A new Multicritical point (in collaboration with V. N. Raja, S. Krishna Prasad, S. Chandrasekhar and B. K. Sadashiva), Proceedings of the 13th AIRAPT Int. Conf. on High Pressure Sciences and Technology, p. 523, edited by A. K. Singh, Oxford and IBH Publishing Co. Pvt. Ltd., New Delhi, (1992).

7. Dielectric studies of hexatic B - smectic A and crystal B - smectic A transitions (in collaboration with C. Nagabhushan, B. R. Ratna, R. Shashidhar and J. W. Goodby), Liquid Crystals **3**, 175, (1988).

8. Phase diagram involving the Twist Grain Boundary phase in the vicinity of a virtual Cholesteric- Smectic A- Smectic C* point (in collaboration with S. Krishna Prasad, V. N. Raja and J. W. Goodby) (to be published).

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